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RESEARCH ON FOG-RESISTANT MATERIALS
FOR HIGH-ALTITUDE HELMET VISORS

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Life Support Systems Laboratory
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NOTICES

FOREWORD

ABSTRACT

Various methods of preventing visibility losses due to fogging of plastic MA-3 and HGU-8/P helmet visors in pressure suits were investigated. Hygrophilic film-forming polymers with polyhydroxyl groups were found to be promising fog-resistant coatings. Their effectiveness depends largely on the relative surface concentration of hygrophilic and hygrophobic groups, since these groups determine the proper balance between wettability and stability of the treatment on prolonged and intermittent exposure to fog-promoting conditions. Visors treated with 83 to 87% hydrolyzed polyvinyl acetate showed good overall optical properties. They exhibited little distortion, and their luminous transmittance and haze values were 92 and 0.4%, respectively. Enhancing the wettability of acrylic surfaces by ultraviolet irradiation and exposure in a thermal column of a nuclear reactor was ineffective. Also, preferential condensation of moisture in the helmet by gas-phase nucleation proved unsatisfactory for inhibiting fogging.

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RESEARCH ON FOG-RESISTANT MATERIALS
FOR HIGH-ALTITUDE HELMET VISORS

I. INTRODUCTION

The increased importance of operating military aircraft at high altitudes and the advent of manned orbital flights pose a number of problems to the personnel of aircraft and space vehicles. Among the factors of considerable importance is the continuous maintenance of optimum visibility conditions for the pilot and crew both within and outside the vehicle.

Severe fogging of high-altitude helmet visors has been encountered on sudden decompression, such as during structural failure of the aircraft canopy and during bailout. Fogging has also been experienced on rapid descent from high altitude. The dangers associated with the partial loss of visibility by flight personnel in high-altitude operations make elimination of fogging in vision devices obligatory.

Various approaches have been used in recent years to accomplish this objective. These methods include: use of a double-wall Thermopane-type visor, utilization of the oxygen supply to sweep the inside of the face mask and to minimize the accumulation of perspiration moisture, heating of the faceplate by resistance wires or electrically conductive transparent coatings, and hygrophilic treatments of the inner surface of the visor to prevent dropwise deposition of water vapor. The effectiveness of these methods varies and is limited by lack of durability (of surface coatings) and by power requirements (of electrically conductive coatings) which may not be satisfied under emergency conditions.

The objective of the present program was to develop effective means of preventing visibility losses due to fogging in plastic helmet visors of pressure suits. In pursuing this objective, investigations were carried out on the nature and the activity of initiation of condensation on preferred sites. Particular attention was given to physical and chemical methods of imparting fog-resistant properties to acrylic surfaces and to the adaptability of these methods to MA-3 and HGU-8/P helmet visors.

II. GENERAL ASPECTS OF FOGGING AND ITS PREVENTION

A. Conditions in a Helmet Enclosure

Fogging can be described as a process in which discrete water droplets from moist air condense on a cold surface. The temperature of the surface must be below the dew point of the vapor-containing air in order for condensation to occur.

The wearer of a helmet is separated from the partly conditioned surroundings of the aircraft or space vehicle, and the water vapor continuously expired by the individual enters into the helmet enclosure. The vapor mixes

with the externally supplied oxygen, and the air space soon becomes saturated with moisture. Under certain temperature conditions the water vapor condenses on the inner surface of the transparent plastic visor of the helmet. The condensate aggregates in minute droplets, which scatter light by refraction and reflection and thus inhibit visibility.

The conditions of heat transfer and condensation in helmet enclosures are complex. To simplify this discussion, the following observations are restricted to water vapor, and effects due to other exhaled gases and to the oxygen supplied for the air space are neglected. The partial pressures of water vapor emitted from the body are 47 and 31 mm Hg; these values correspond to the temperature of the expired air (37°C) and of the skin (29.5°C), respectively. On a reasonably clean adsorbent, condensation does not occur unless the temperature of the surface is below the dew point of the moisture-saturated system. When the environment is in thermal equilibrium with the human body, the dew point approximates body temperature. When the temperature of the environment is below that of the water vapor emitted into the helmet enclosure, the process of heat exchange initiates condensation.

The rate of condensation increases with increasing temperature difference, and therefore severe fogging is associated with low environmental temperatures. If external cooling causes the temperature inside the helmet enclosure to drop to 65 to 75°F, which corresponds to vapor pressures of 15 to 22 mm Hg, approximately half of the physiologically generated water vapor will condense in the air space in the form of droplets. This fog precursor can be carried by convection and be deposited on nontransparent parts of the helmet or it can diffuse through nonturbulent air toward the visor. Upon moving toward the cold surface of the visor, the vapor-air mixture will gradually cool and form additional airborne fog particles. Because of the small initial size of these droplets, their equilibrium water vapor pressure will be higher than the water vapor pressure for a continuous film, in accordance with Kelvin's relationship:

$$\ln \frac{P}{P_O} = \frac{2 \sigma M}{r \, d \, R \, T} \tag{1}$$

where

P   is vapor pressure of the droplet

P_O is saturation water vapor pressure

σ   is surface tension of the droplet-forming liquid

M   is molecular weight of the droplet-forming liquid

r   is radius of the droplet

d   is density of the droplet

R   is the gas constant

T   is absolute temperature.

Although the fog precursor could resist aggregation in the air space of the helmet, it would not escape condensation on the visor because of the thermodynamically favored decrease in the free energy of the system and the associated reduction in the vapor pressure of the condensate upon deposition on a

cooler surface.

Thus fogging of a helmet visor occurs by direct condensation of moisture on the plastic surface or by attachment of airborne droplets. Interference with visibility results from the growth of these droplets to a size comparable with the wavelength of light. Whether deposition of airborne droplets or primary condensation is the main source of fogging depends on the interrelationship between temperature, turbulence, and relative surface area of the visor and the inner wall of the helmet.

B. Some Approaches Used to Prevent Fogging

The manner in which fog droplets form affects coalescence and thus has a bearing on the severity of fogging. The condensation mechanism involves formation of water droplets on active sites where enough molecules come together to produce an embryonic liquid phase. Once such embryos are formed, more rapid condensation takes place on these sites, and eventually large visible drops develop. If the free energy of the solid on which condensation occurs is high at the solid-air interface and if the surface tension of the droplets is small, coalescence is favored. Under coalescence conditions it is possible to improve the optical properties of a vision device exposed to differential temperature and humidity conditions.

Thus, the problem of overcoming fogging in high-altitude helmets can be approached by two methods: (1) by inhibiting formation of water droplets and their deposition on the visor and (2) by inducing coalescence of already formed droplets in order to obtain a continuous film of condensate on the visor. The first method is concerned with maintaining unfavorable conditions for condensation of water vapor within the helmet, in particular, on the inner surface of the visor. This can partly be achieved by heating the visor; by using appropriate design features to increase the volume, air supply, and venting of the helmet; and by using moisture precipitators. The second approach, which was emphasized in this research, involves modification of the surface of the visor by chemical treatment.

Many organic compounds for the prevention of fogging of glass and transparent plastics have been developed commercially. Among these are sulfated aliphatic hydrocarbon derivatives (ref. 1), monoesters of ethylene glycol (ref. 2), esters of sulfopolycarboxylic acids (ref. 3, 4), mixtures of gelatin and cellulose nitrate in an acetic acid medium (ref. 5), and formulations consisting of a surfactant, such as polyoxyethylene sorbitan monostearate (Tween 61) and mineral spirits (ref. 6). The effectiveness of these compounds depends essentially on their hygrophilic nature, which promotes wettability of the treated substrate and thereby enhances deposition of water vapor in a continuous film rather than in vision-impairing droplets.

The wettability of the surface of a solid is determined by the following relationship:

$$\cos \theta = \frac{F_{S/A} - F_{S/L}}{\gamma_{L/A}} \tag{2}$$

where

θ is the contact angle

$F_{S/A}$ and $F_{S/L}$ are the interfacial energies of the solid at the solid-air and the solid-liquid boundaries, respectively

$\gamma_{L/A}$ is the surface tension of the liquid at the liquid-air interface.

The effectiveness of a given treatment in promoting deposition of a uniform film of condensate on the surface of the substrate depends, therefore, on the extent to which it alters the equilibrium condition of Eq. 2 toward higher values of $\cos \theta$.

A diametrically opposed approach to the use of hygrophilic substrates is the use of hygrophobic substrates. The underlying concept is that fogging will not occur if airborne droplets do not adhere to the substrate and if nucleation of the primary condensate on the surface of the solid is prevented. The use of silicones (ref. 7) to impart hygrophobicity to aircraft windows (ref. 8) has not been found successful. It was shown that nucleation sites, however small their number, induce condensation (ref. 9) on a hygrophobic surface such as paraffin. The thermodynamic basis of this finding is the relationship between the energy of nucleation and the contact angle of wetting (ref. 10). Under conditions of perfect nonwetting the energies of nucleation at the surface and in the air space are identical. If there is slight interaction between the droplet and the surface of the solid, as is usually the case, the contact angle is always less than its limiting, nonwetting value. Consequently, nucleation at the surface should occur more readily than in air.

Ordinarily, nucleation in air is greatly promoted by dust and ionization. Theoretically, it is possible to have a condition in which slight supersaturation does not initiate nucleation on a hygrophobic surface. This delicate balance, however, cannot be maintained at higher degrees of supersaturation. It can be calculated from Kelvin's equation (1) that water droplets larger than 8 to 10 A (a very small cluster of molecules) tend to grow under conditions of saturation in the absence of surface-active substances. If such droplets were the main cause of fogging in a closed system, it might be possible to utilize electrostatic surface effects to repel the condensate. However, this approach might not be effective because water droplets usually carry charges of either polarity.

All things considered, it appears that promotion of water-vapor condensation on the surface of vision devices offers better possibilities for the prevention of fogging than inhibition of condensation. However, many hygrophilic treating compounds have limited antifogging effectiveness on prolonged or intermittent exposure to high humidity. This limitation is a consequence of the pronounced moisture sensitivity of these materials; not only is surface wetting enhanced but also dissolution of the treating agent in the condensate and subsequent loss of activity are promoted.

In the course of investigations performed in this research, it was found that certain shortcomings of fog-resistant formulations could be

avoided by the use of a film-forming polymer coating with properly balanced hygrophilic and hygrophobic groups. This balance provided the desired surface concentration of hygrophilic condensation sites for deposition of a film of water and at the same time maintained moisture stability of the coating through the hygrophobic groups and the higher molecular weight of the compound.

III. EQUIPMENT AND METHODS

A. Fog-Testing Apparatus

To determine the effectiveness of antifogging treatments in preserving the optical quality of acrylic surfaces under the temperature and humidity conditions encountered in the helmet enclosure and its surroundings, an appropriate testing apparatus had to be developed. The principle on which the design of this apparatus was based involved determination of the degree of optical resolution of a line pattern photographed through a treated acrylic window which formed a partition between a cold-dry and a warm-humid chamber. Due to heat transfer through this partition, moisture condensed on the surface facing the humid compartment. This condensation produced a measurable change in the optical quality of the photographed pattern.

The equipment, shown in Fig. 1, consists of a dual chamber, C, insulated with Styrofoam. One compartment is maintained at a fixed temperature of 95°F and a variable humidity of 10 to 95% r.h. The other compartment is continuously flushed with dry air, and the temperature is regulated between -50 and +75°F by a voltage divider which controls the power input to a heating element, E. The heating element is interposed between the variable-temperature compartment and an air-refrigerating unit, R. R consists of a precooling vessel (immersed in a dry ice-isopropanol bath) with a copper coil wound around it and a 5-in.-thick Styrofoam box which houses the cooling system and provides thermal insulation from the surroundings. The air is admitted to the refrigerating unit from a drying column, D, which consists of a 6-in.-diameter 4-ft-long flanged pipe filled with 60 lb of anhydrous calcium sulfate. The use of a desiccant was necessary, because, without it, the air (at a flow rate of 3 cfm) lost a substantial amount of water due to refrigeration. This water formed a thick coating of ice on the walls of the precooling vessel and clogged the air inlet after 4 hr of operation.

The dried air is conveyed through a needle valve, V, and flow meter, F, to the refrigerating unit, R. From here it is introduced into the cold chamber, C. The air supply for the moisture-controlled antechamber, K, is provided by an air tank, T, which conveys a dry airstream through a twin tap into a moisture saturating bath, M. From the bath the air flows into the moisture-conditioned chamber in an amount controlled by a solenoid valve arrangement (discussed later) actuated by an electrolytic hygrometer, H.

A closer view of the humidity chamber is shown in Fig. 2. Control of the temperature range of 77 to 100°F is provided by an air-circulating blower, B, which conducts the airstream through a Nichrome wire heater,

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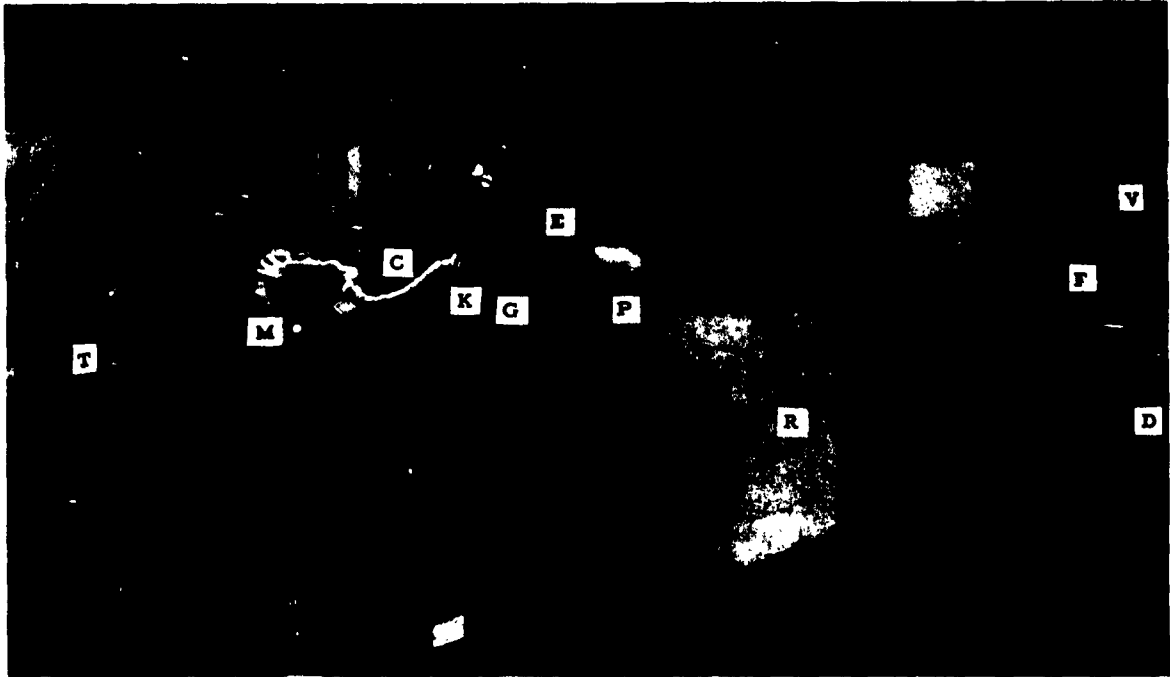
Figure 1
Fog-Testing Apparatus

C, dual chamber
D, drying column
E, delivery tube
F, flow meter
G, glass window
K, moisture-controlled antechamber

M, moisture saturating bath
P, camera
R, air-refrigerating unit
T, air tank
V, needle valve

Figure 2
Close View of Humidity Cabinet and Moisture-Control Unit

B, air-circulating blower
E, delivery tube
H, electrolytic hygrometer
K, moisture-controlled antechamber
M, moisture saturating bath
S, plastic specimen
W, wattmeter

controlled by a power rheostat. Early in the course of this study we observed that the glass window, G, invariably fogged from the inside at high humidities, thereby interfering with the line-resolution study of the plastic specimen, S. To alleviate this problem, a stream of heated air was flushed against the glass window through a delivery tube, E, which warmed the glass above the dew point, thus keeping the window fog-free.

The cold-dry and warm-humid compartments, separated from each other by foamed polystyrene, are provided with a 4 x 5-in. partitioning frame which accommodates test specimens and subjects them to the desired temperature and humidity conditions. Copper/constantan thermocouples, located near the heating element in the cold chamber and in surface contact with the plastic sheet on either side of the partition, permit determination of the temperature in important areas of the apparatus. The temperature conditions in different sections of the cabinet are shown in Fig. 3.

B. Controlled-Humidity Apparatus

To eliminate variation in atmospheric conditions in the antechamber, K, a humidity-controlled environment was used. The twin airflow method (ref. 11 and 12), in which airstreams of dry and moisture-saturated air are mixed in desired proportions to furnish an atmosphere of the required humidity, was utilized for the air-supply system. The assembly is shown in Fig. 4. An air tank, T, is provided with a Y tap. One arm of the tap supplies air through a solenoid valve, V, to two moisture-saturating tubes, S; while the other enters a molecular-sieve drying column, D. Saturation of the airstream with moisture is achieved by bubbling the gas in water through fritted glass discs. The discs are maintained in a constant-temperature bath, B.

The wet airstream, relieved of excess water in a glass-wool trap, G, and the dry air are introduced to the chamber, where they are mixed. An Aminco-Dunmore hygrometer, covering the range of 5 to 95% r.h., is used as a humidity indicator and regulator in conjunction with a 20-mv d.c. recorder-controller. To improve the precision of humidity control by the solenoid valve, the relative flow rates of dry and wet air are adjusted to maintain desired conditions without the help of the automatic switching device.

In operation, a continuous stream of dry air is admitted to the antechamber at a rate depending on the humidity desired. At the same time, moisture-saturated air is circulated in the chamber until its flow is interrupted by the magnetic valve, which switches into the off position. The valve is actuated by a control relay, preset at the upper value of the humidity limit. The flow of moisture-saturated air is resumed when the humidity reaches the lower control value, at which point the solenoid valve reopens. This method permits continuous control of humidity within $\pm 1.5\%$ for the 20 to 95% r.h. testing range.

C. Optical Method for Determining Fog Resistance of Acrylic Windows

A photographic method was used to determine the effectiveness of
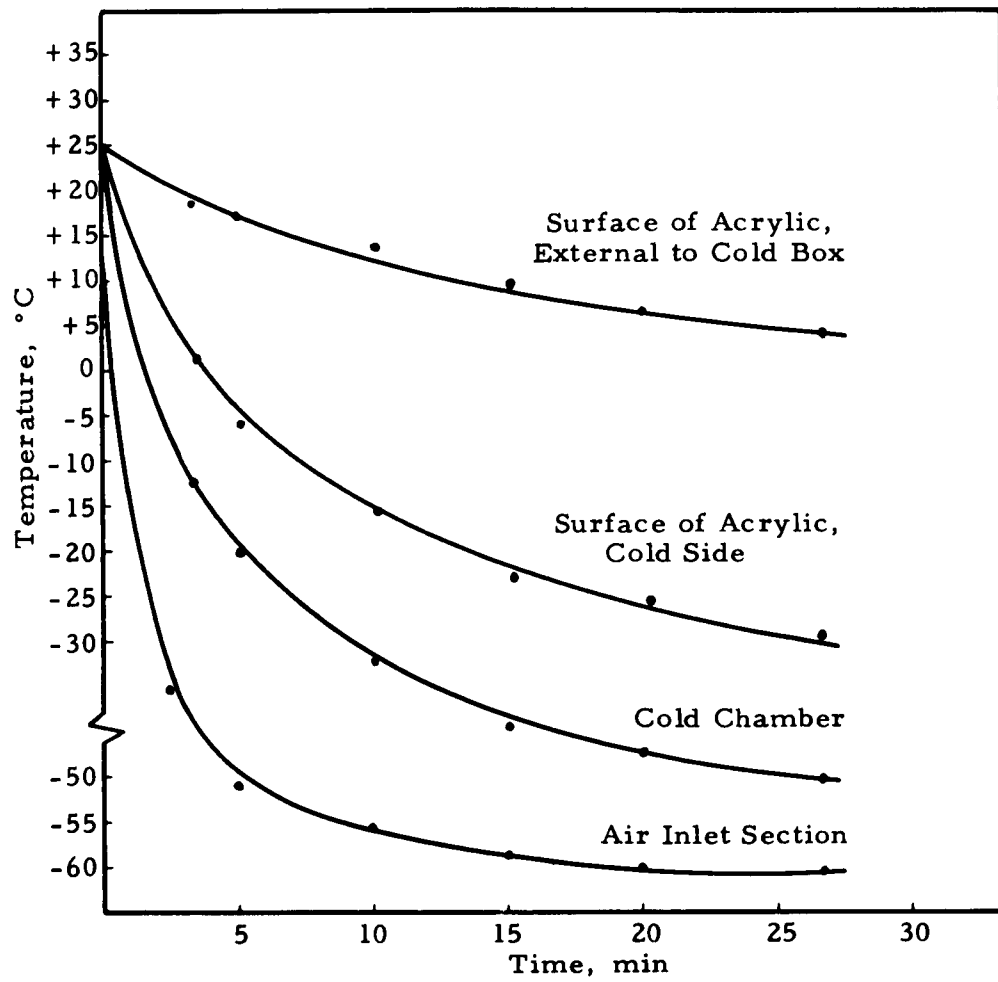
Figure 3
Cooling Rate in Different Sections of the Conditioning Cabinet
at 3-cfm Airflow

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Figure 4
Variable-Humidity Air-Supply Unit

B, constant-temperature bath   V, solenoid valve
D, molecular-sieve drying column   Y, Y tap
G, glass-wool trap   T, air tank
S, moisture-saturating tube

antifogging treatments for acrylic visors. In this procedure a resolution pattern is placed in the cold section of the cabinet and photographed after the test specimen is introduced between the camera lens and the object. The camera (Polaroid Corporation), P (Fig. 1), is mounted on a fixed support attached to the viewing window of the humidity-conditioning cabinet. Two 7-w bulbs illuminate the line pattern.

The line pattern is an optical resolution chart developed by the National Bureau of Standards (ref. 13) to determine the quality of lens systems. It comprises an array of vertical and horizontal lines whose spacing on the photographic image ranges from 3 to 80 lines/mm when the distance between the lens and the object is 26 times the focal length of the lens. The condition of incipient merging of the line pattern, determined by inspection of the photograph with a suitable magnifying glass (12x), provides a measure of the resolution of the optical system. Since this test is used as a criterion in quality rating of photographic equipment, it is admittedly over-sensitive for determining the optical acceptability of antifogging treatments. However, the test greatly facilitates selection of the best treatments from a series of relatively effective antifogging compounds.

A preliminary investigation of surface-treated acrylic windows at room conditions (75°F, 40% r.h.) showed considerable differences in the resolving power of the optical system. These effects are shown in Fig. 5, 6, and 7, which show photographs of the line pattern for untreated, polyvinyl alcohol-coated, and Nylon emulsion-coated acrylic (Plexiglas), respectively. It should be understood that the reproduced photographs (Fig. 5, 6, and 7) lose sharpness in comparison with the resolution of the original image. The resolution pattern obtained for the clear acrylic sheet was 13.0 lines/mm, while that for the PVA-coated specimen was 11.2 lines/mm. Although the polyvinyl alcohol coating did not greatly affect the transparency of the sample, the image was distorted as a result of uneven deposition of the surface film. The poorest resolution, 2.6 to 3.8 lines/mm, was obtained with Nylon (Gental, General Dispersions, Incorporated) emulsion-coated specimens, which exhibited a foglike haziness on drying.

In the actual evaluations of the antifogging effectiveness of given treatments, the resolution pattern through the treated window was photographed at frequent intervals while the window was being subjected to conditions promoting water-vapor condensation. Any changes in resolution were then determined by inspection of the photographs, and the test duration and the temperature and humidity conditions associated with these exposures were carefully noted.

D. Cold Stage for the Study of Condensation of Water Vapor on Acrylic Substrates

To determine the distribution, activity, and concentration of discrete condensation sites on untreated and treated acrylic surfaces, a microscopic study of the condensation process was initiated. The apparatus consisted of a Thomas-McCrone cold stage, which permitted passage of cold dry air on the bottom and warmer moist air along the top of a plastic test specimen. Provision was made for insertion of thermocouples to measure temperatures
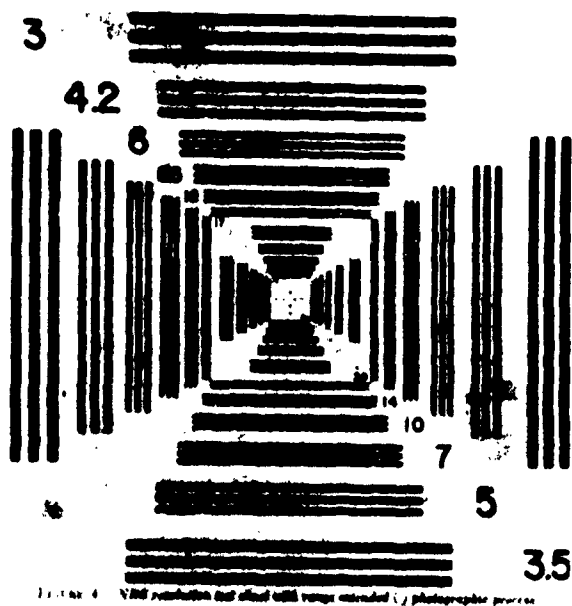
Figure 5
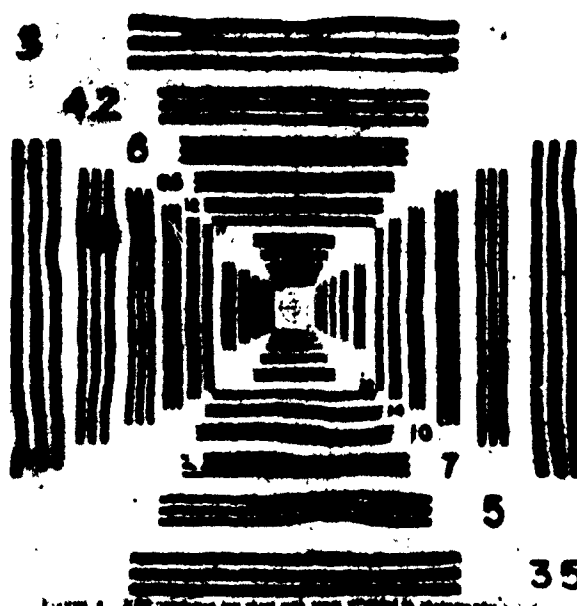Resolution Pattern
of the Untreated Acrylic Window

Figure 6
Resolution Pattern
of the PVA-Treated Acrylic Window

Figure 7
Resolution Pattern
of the Nylon Emulsion-Coated Acrylic Window

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at opposite surfaces of the sample. Figure 8 shows the design of the stage, while Fig. 9 presents the flow control system for the two airstreams.

The procedure was as follows. A thermocouple bead was attached to the top and bottom surfaces of the plastic sample by gluing with an ethylene dichloride-Lucite mixture. After drying, the assembly was placed in the cold stage and put on the microscope. The objective lens barrel was used to seal the top air path. The air pump was turned on, and airflow through the coil submerged in dry ice-acetone was sent across the bottom surface of the sample. A dry warm airstream was pulled across the top surface, and the temperature of the top surface was stabilized by controlling the flow of this stream. When equilibrium temperatures were attained, moisture was added to the top airstream, and drop size and spacing were measured.

E. Method for Inducing Water-Vapor Condensation by Nucleation

The possibility of partially diverting condensation of water vapor on the visor by promoting coalescence of airborne water droplets in the vapor phase was investigated in the apparatus shown in Fig. 10. The equipment consists of a humidifying section, a visor chamber simulating the environment of the helmet, a salt nuclei generator, and a thermostatically controlled conditioning box.

The main airstream, which is first filtered and humidified, is mixed with the salt aerosol and then admitted to the visor chamber at approximately 0.3 cfm. The aerosol is generated by passing cool air over an electrically heated platinum wire coated with sodium chloride crystals. A current is passed through the wire at such a rate as to vaporize the salt, which upon cooling condenses into nuclei approximately 1μ in diameter.

The chamber is cooled to a temperature such that water vapor from the humidified air condenses on the visor. The temperatures of the cold box and the inner surface of the visor are measured by iron/constantan thermocouples placed at convenient locations on the outer and inner surfaces of the chamber. The nucleated gas stream leaving the chamber is heated, passes through an electrostatic precipitator, and then passes through an electric hygrometer. The removal of the salt nuclei from the airstream by an electrostatic precipitator is a precautionary measure to prevent contamination of the sensitive hygrometer.

The hygrometer was used to determine the quantity of water vapor removed by the salt nuclei. The relative humidity and the temperature of the airstream were measured before the air entered the visor section and before and after nucleation. The size of the salt nuclei was determined from the average size of particles impacted on a glass slide. A General Electric nuclei counter was used to determine the concentration of the nuclei in the gas stream.

F. Coating Assembly for Helmet Visors

To deposit a uniform film of controlled thickness on the surface of MA-3 and HGU-8/P helmet visors, a dip-coating apparatus utilizing the screw-drive mechanism of the Instron testing machine was devised. The
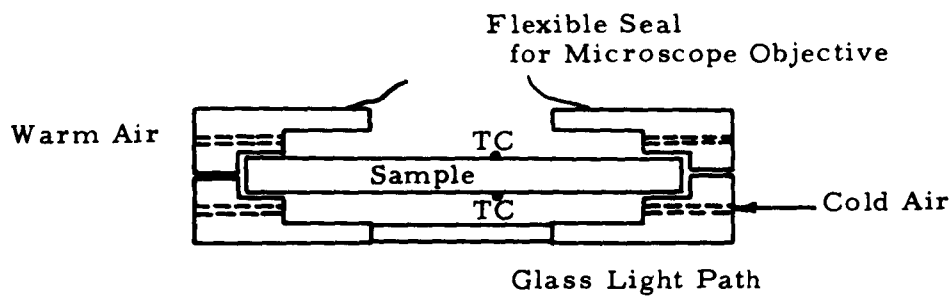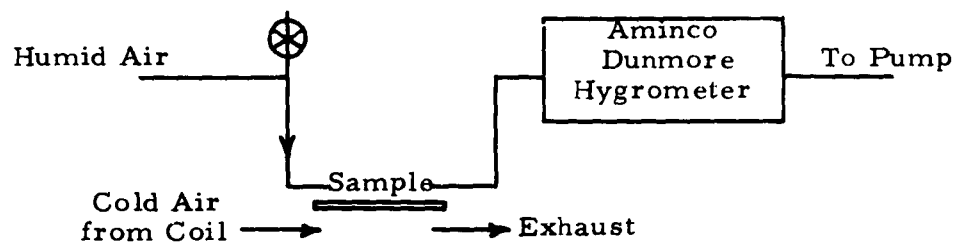
Figure 8
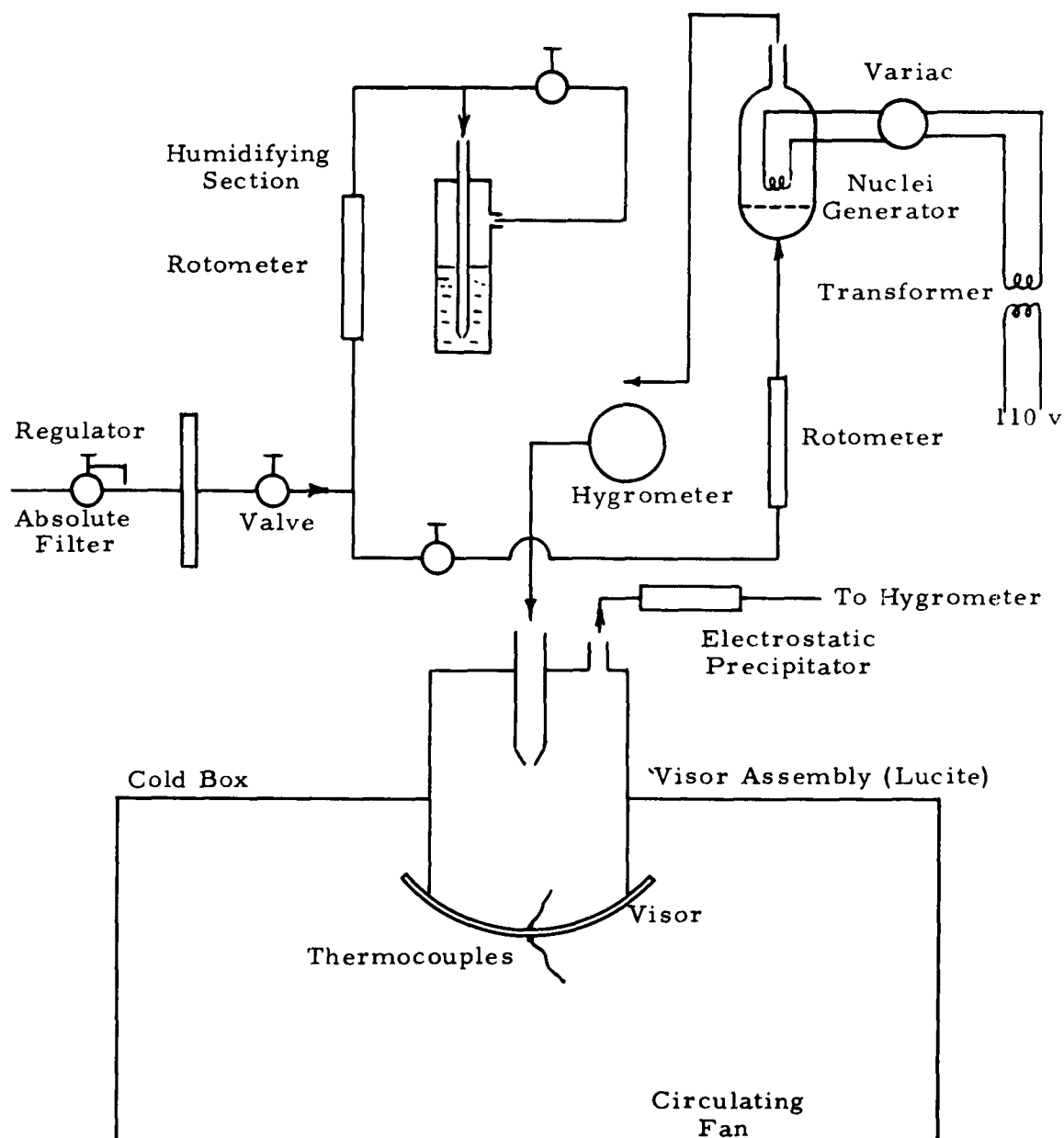Design of the Cold Stage

Figure 9
Flow Controls for the Cold Stage

Figure 10
Apparatus for Removal of Water by Gas-Phase Nucleation

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assembly, shown in Fig. 11, consists of a glass tank, T, holding the coating solution, and a visor holder, H, mounted on the crosshead of the Instron. In operation, the visor is dipped into the solution to the upper mounting rim and is subsequently withdrawn at a rate ranging from 0.1 to 0.5 in./min, depending on the viscosity of the system. In most applications with nongelling solutions, a withdrawal rate of 0.5 in./min proved satisfactory for deposition of a clear undistorted film of the antifogging compound.

IV. EXPERIMENTAL DATA AND DISCUSSION

The substrate employed in most of the work was Plexiglas 55 (Rohm and Haas Company) acrylic sheet of 0.20-in. thickness, as used in MA-3 and HGU-8/P helmet visors. Studies of susceptibility to fogging were conducted on appropriately treated 5-3/8 x 3-5/8 in. windows prepared from this material as well as on cylindrical visors (for MA-3 helmets).

A. Treatment with Surface-Active Compounds

To determine the effectiveness of wetting agents in imparting fog resistance to acrylic surfaces, a number of surfactants were investigated. Cationic surfactants of the tertiary amine type (Ethomeen C/12, Armour Industrial Chemical Company),

$$RN \begin{matrix} (CH_2CH_2O)_x \\ \\ (CH_2CH_2O)_y \end{matrix}$$
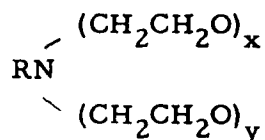
anionic phosphate esters (Gafac RE 610, Antara Chemicals), and nonionics such as ethoxylated nonylphenols (Polytergent B-200 and B-350, Olin Chemical Corporation) and polyethylene glycol alkylphenyl ethers (Nonic 300 and 218, Pennsalt Chemicals Company) were studied.

Polytergent B-350 and Nonic 218, selected in preliminary investigations as promising, were subjected to more detailed evaluations. These nonionic compounds were applied to the acrylic windows by spraying with an air brush. The excess was removed from the plastic by wiping with lintless lens paper. The treated windows were exposed at 25.5°C to a controlled humidity of 50% r.h. for 4 hr. The surface temperature of the acrylic in the humidity chamber was gradually lowered to slightly below freezing.

Although consideration of the relationship between relative humidity and water vapor pressure indicated incipient water and condensation on the plastic surface at a temperature of 20.7°C, no fogging was noticed on test specimens exposed to lower temperatures at the selected humidity. The series of pictures in Fig. 12 presents the resolution of the line pattern photographed through the treated windows, and the data are summarized in Table 1.
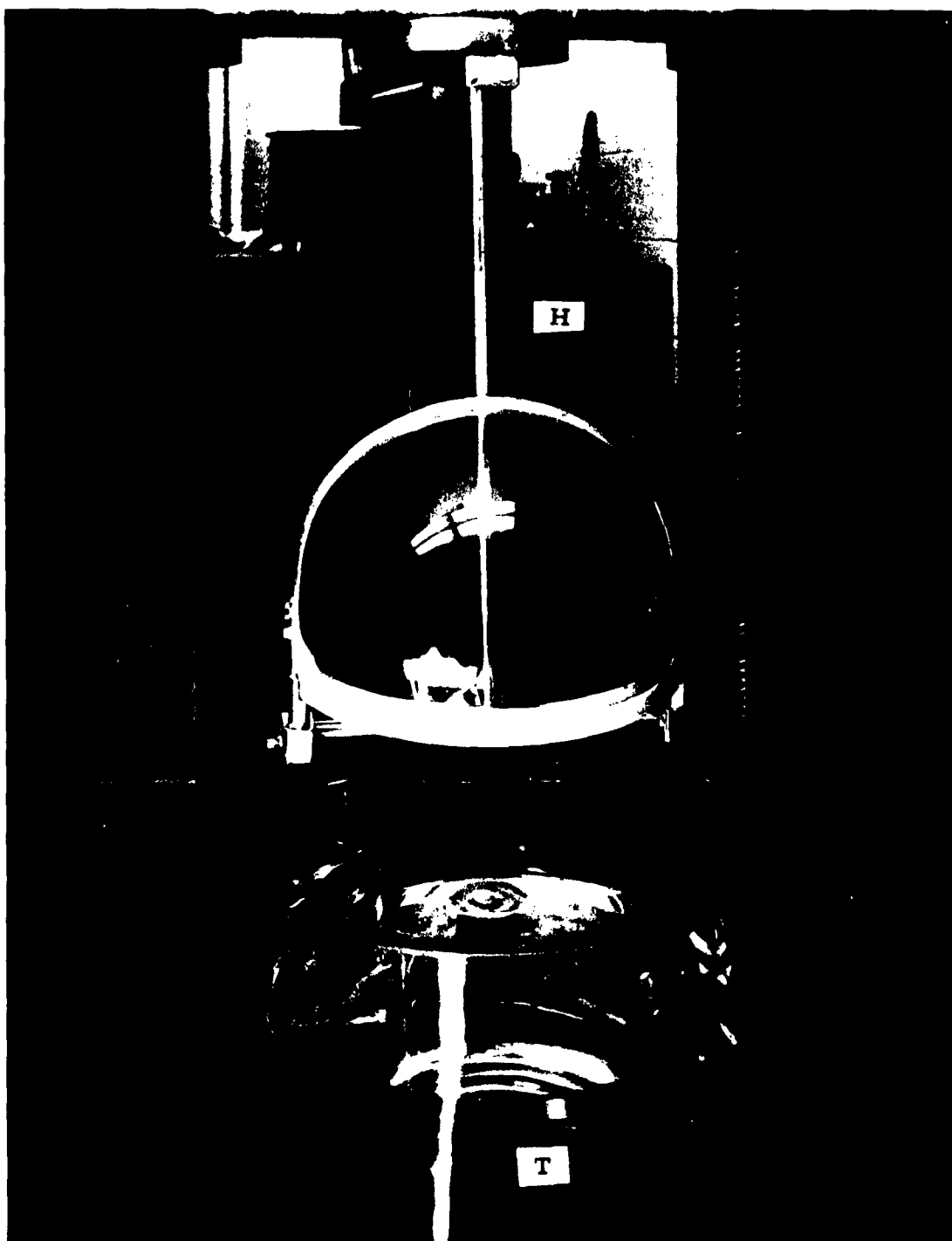
Figure 11
Dip-Coating Apparatus

a. 25°C   b. 4°C
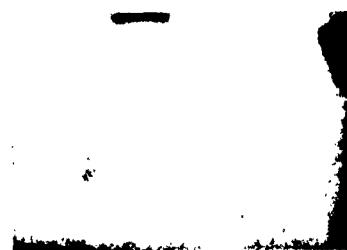
c. 2°C   d. 0°C

e. -1°C   f. -2°C

Figure 12
Resolution Patterns of Surfactant-Treated Acrylic Windows
at 50% r. h. and Temperatures from +25 to -2°C

Left side of each photograph: Polytergent B-350
Right side of each photograph: Nonic 218

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Table 1

RESOLUTION OF SURFACTANT-TREATED ACRYLIC WINDOWS
AT 50% R. H. AND TEMPERATURES FROM +25 TO -2°C

Fig.	Surface Temperature, °C	Resolution, lines/mm	
		Polytergent B-350	Nonic 218
12a	25	10	9
12b	4	9	8
12c	2	9	7
12d	0	8	7
12e	-1	2	2
12f	-2	0	0

The fog resistance of the surfactant-treated acrylic window was maintained over a considerable temperature range while water continuously condensed on the window without appreciably impairing its optical properties. At -1°C, however, the visibility was greatly reduced; the aqueous solution of the surfactant froze and the surfactant precipitated on the window surface. This condition occurred after 2 hr of cooling, when the temperature on the inside of the window was -33°C (-27°F). Although the surfactant enhanced wettability and a film condensed on the acrylic, exposure of a once-used specimen to a high humidity resulted in its fogging. This suggested that brief exposure to moisture removed the surfactant.

B. Irradiation of Acrylic Windows

In an effort to produce a permanent change in surface properties of helmet visors, particularly in regard to increasing the number of condensation sites and the surface reactivity, acrylic windows were subjected to ultraviolet and gamma irradiation. Specimens were exposed to a high intensity ultraviolet source for 15 min to 5 hr. The fog resistance imparted by this treatment was negligible, even in those samples which received the maximum dose of 1.8×10^3 joules cm^{-2}. Irradiation of acrylic windows in a thermal column of a nuclear reactor maintained for 6 hr at 60 kw was also ineffective. Specimens which received a dose of 1.03×10^{10} neutrons cm^{-2} sec^{-1}, equivalent to an integrated flux of 2.2×10^4 neutrons cm^{-2}, exhibited a yellow discoloration similar in apperance to visors treated with electrically conductive coatings. The light transmission curves for the irradiated and unirradiated acrylic are shown in Fig. 13.

C. Treatment with Tetraisopropyl Titanate

Tetraisopropyl titanate has been used to promote uniform condensation of water on Mylar sheeting in greenhouses (ref. 14). The effectiveness of this treatment is attributed to the deposition of hygrophilic titanium dioxide on the nonwettable substrate.

A 5% solution of tetraisopropyl titanate (E. I. du Pont de Nemours and Company) in anhydrous petroleum ether was sprayed on the surface of acrylic windows. After exposure to atmospheric humidity the compound was hydrolyzed, leaving a fine deposit of titanium dioxide on the substrate.
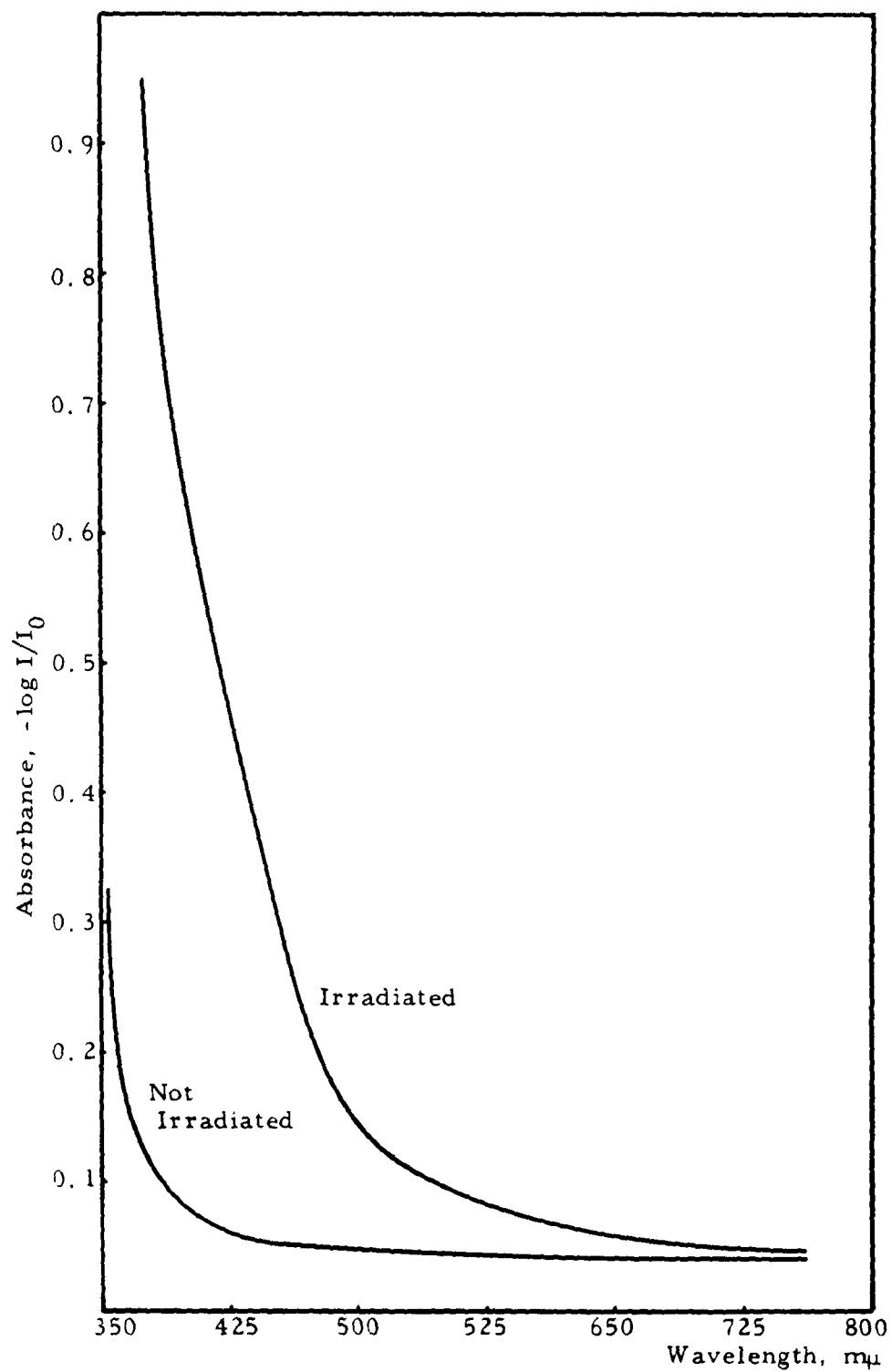
Figure 13
Light Transmission through Irradiated Acrylic Windows

$$Ti(OR)_4 + 2H_2O = TiO_2 + 4ROH \qquad (3)$$

Although the treated surface was well wetted when immersed in water, in contrast to the untreated surface, from which water rolled off after immersion, the titanium dioxide deposit did not prevent fogging on exposure to high humidity. This behavior could be the result of a paucity of condensation sites. The size of the titanium dioxide deposit is macroscopic in comparison with the much larger surface concentration of hygrophilic groups on organic wetting agents.

D. Screening of Hygrophilic Polymers for Fog-Resistant Coatings

To utilize the lessened susceptibility of high-molecular-weight compounds to desorption and to ultimate removal from a substrate, a number of film-forming polymers were considered for antifogging treatment of acrylic visors.

The polymers investigated first were: methyl cellulose (Methocel 65 HG, Dow Chemical Company), polyacrylamide (Cyanogum 41, American Cyanamid Company), gelatin (Viscomix, Swift and Company), and a carboxylated vinyl polymer (Carbopol 934, B. F. Goodrich Chemical Company). Aqueous solutions of Methocel 65 HG (2%), gelatin (Viscomix) (1%), Carbopol 934 (0.3%) and Cyanogum 41 (10%), each containing 0.1 to 0.5% of nonionic surfactant (either Polytergent B-350 or Nonic 218), were applied to surfactant pretreated acrylic windows by spraying, casting, or dip-coating. The spray method provided a coating of better optical quality than cast films, which had a tendency to develop hairlike ridges at the surface, apparently as a result of film shrinkage on drying. The best results were obtained by the dip-coating method carried out at a withdrawal rate of 0.1 in./min. However, none of the coating systems proved entirely satisfactory, as indicated by fog tests performed at 75% r.h. at a temperature differential of 65°C (+35 and -30°C in the box and antechamber, respectively).

Although the appearance of most of the coated acrylic sheets was not perceptibly affected by the treatment, the Cyanogum-coated windows exhibited a spotted surface at 20% r.h. and 25°C. This undesirable optical condition disappeared when the sample was introduced to an environment of high humidity (90% r.h.). However, prolonged exposure again resulted in decreased visibility through the window. Carbopol 934 showed little antifogging activity. Although Methocel 65 HG was effective initially, it lost its fog-resistant properties on reexposure to humidity after drying. The Viscomix film provided a wettable surface. However, the material appeared to age on drying, as indicated by microscopic cracks which resulted in powdering of the coating. This powder was carried away by condensing water vapor, leaving unprotected areas on the surface of the acrylic sheet and thereby initiating fogging of the window.

Attempts to utilize alginates (Kelcoloid LVF, Kelco Company) and solvent-complexing N,N-dimethyl amides (C. P. Hall Company) proved unsatisfactory. Similarly, a 20% isopropanol solution of a water-soluble acrylic polymer (Carboset 511, B. F. Goodrich Chemical Company) did not

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offer protection against fogging, although the generic similarity between the coating and the substrate seemed particularly promising in regard to the adherence and stability of the treatment.

The film-forming polymer which exhibited relatively good optical and fog-resistant properties was PVA. Aqueous solutions containing 10% each of Lemoflex 29-13 (Bordon Chemical Company), Elvanol 72-60 (E. I. du Pont de Nemours and Company), and Gelvatol 20-30 (Shawinigan Resins Corporation), differing in water solubility and viscosity were prepared for dip-coating of acrylic windows. Of these, the low-viscosity Gelvatol, assayed at 89% hydrolysis, appeared the most promising. Fogging tests performed over extended periods (5 hr) at a controlled humidity of 50% r. h. and an interior and exterior temperature of +25 and -20°C, respectively, did not produce adverse optical effects despite the copious condensation which ran off the surface of the specimen. Reexposure of the treated sample to humidity after drying, however, resulted in fogging of the acrylic window.

E. Modification of PVA Coating Systems

The relatively good optical properties of PVA-treated acrylic windows in the dry state as well as on exposure to conditions promoting water-vapor condensation indicated the desirability of utilizing this hydrophilic polymer in fog-resistant coatings for helmet visors. However, fogging of treated windows in repeated wetting-drying cycles suggested modification of the coating system in order to impart better durability to the treatment. Several approaches were selected to achieve this objective.

1. Preparation of Thermally Reversible Gels

Preliminary attempts to tie PVA in a three-dimensional network aggregate were made with Congo red as the gelling agent. This diazo compound, used in an amount less than 0.5% in a 10% aqueous solution of PVA, provided a thermally reversible gel in the range of 24 to 65°C. Although films deposited on acrylic windows from the fluidized PVA-Congo red formulation retained their antifogging effectiveness after rinsing with water, the deep red tinge imparted to the transparent coating by the dye was objectionable from the viewpoint of light-transmittance requirements set in the specifications for helmet visors.

For this reason efforts were directed toward the formation of a colorless and transparent PVA gel. The use of boric acid in the PVA solution and subsequent pH adjustment of the system satisfied this condition. A similar effect was also obtained with sodium tetraborate ($Na_2B_4O_7 \cdot 10H_2O$). Addition of a 10% aqueous solution of sodium tetraborate to a hot (74°C) 5% aqueous solution of Gelvatol 20-30 provided a colorless gel at room temperature (23°C). The gelling reaction presumably involves formation of a didiol complex, according to Devel and Neukom (ref. 15).

$$\text{(PVA structure)} + Na_2B_4O_7 \cdot 10H_2O \rightleftharpoons \text{(borate ester complex)} \quad (4)$$
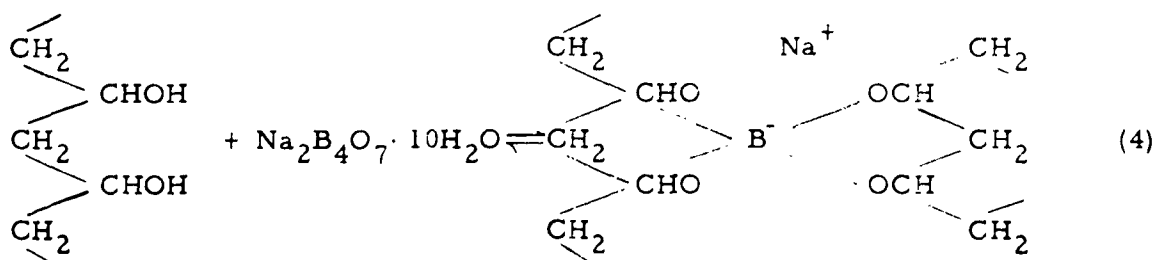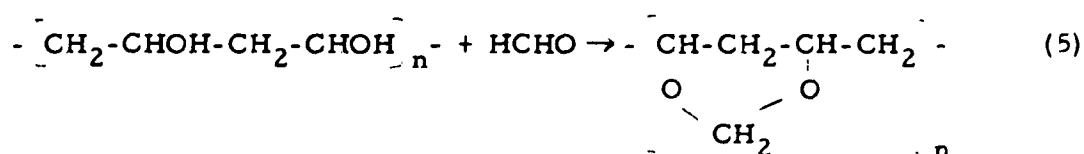
The dip-coating of acrylic windows with the modified PVA solution was unsatisfactory because the freshly deposited films showed a tendency toward optical distortion. Although initial fogging of samples was inhibited, distortion became more severe on multilayer adsorption of water vapor. Presumably this distortion is a result of immediate gelation upon withdrawal of the substrate from the coating bath. Attempts to minimize this difficulty by infrared heating of the acrylic windows during the coating process proved unsuccessful. The radiant heat promoted film formation at the surface of the bath, thus interfering with uniform coating of the substrate.

2. Partial Blocking of Hydrophilic Sites on PVA

Another approach to increase the water resistance of PVA films is to partially react the available hydroxyl groups of the polymer with selected organic compounds.

A commercial urea-formaldehyde compound, Resloom E-50 (Monsanto Chemical Company), was used in a coating formulation containing 20% of the additive by weight of PVA. The hydrophilic properties of this modified coating solution were appreciably reduced in comparison with PVA, as indicated by the pronounced fogging tendency of treated acrylic windows (Fig. 14). The dropwise deposition of water vapor on the surface of the plastic occurred on the first exposure to the condensing adsorbate, as shown in the progressively deteriorating visibility through the windows (Fig. 14a, b, c). This result, in comparison with the good wettability of PVA films under similar conditions, suggested excessive reaction of hydroxyl groups with the insolubilizing agent.

Less extensive blocking of hydrophilic sites was attempted in an incomplete reaction of PVA in a 20% aqueous solution with 1.8% formaldehyde by weight of PVA. Under suitable conditions formaldehyde reacts with PVA to yield polyvinylformal.

$$-[CH_2-CHOH-CH_2-CHOH]_n- + HCHO \rightarrow -\left[\underset{\underset{CH_2}{\diagdown O \quad O \diagup}}{CH-CH_2-CH-CH_2} \right]_n- \quad (5)$$

This reaction was carried out at 70°C for 6 hr. Acrylic windows treated with the resulting solution diluted to 10% modified PVA exhibited good optical and antifogging characteristics on initial exposure to moisture and in repeated wetting-drying cycles, as shown in Fig. 15.

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Figure 14
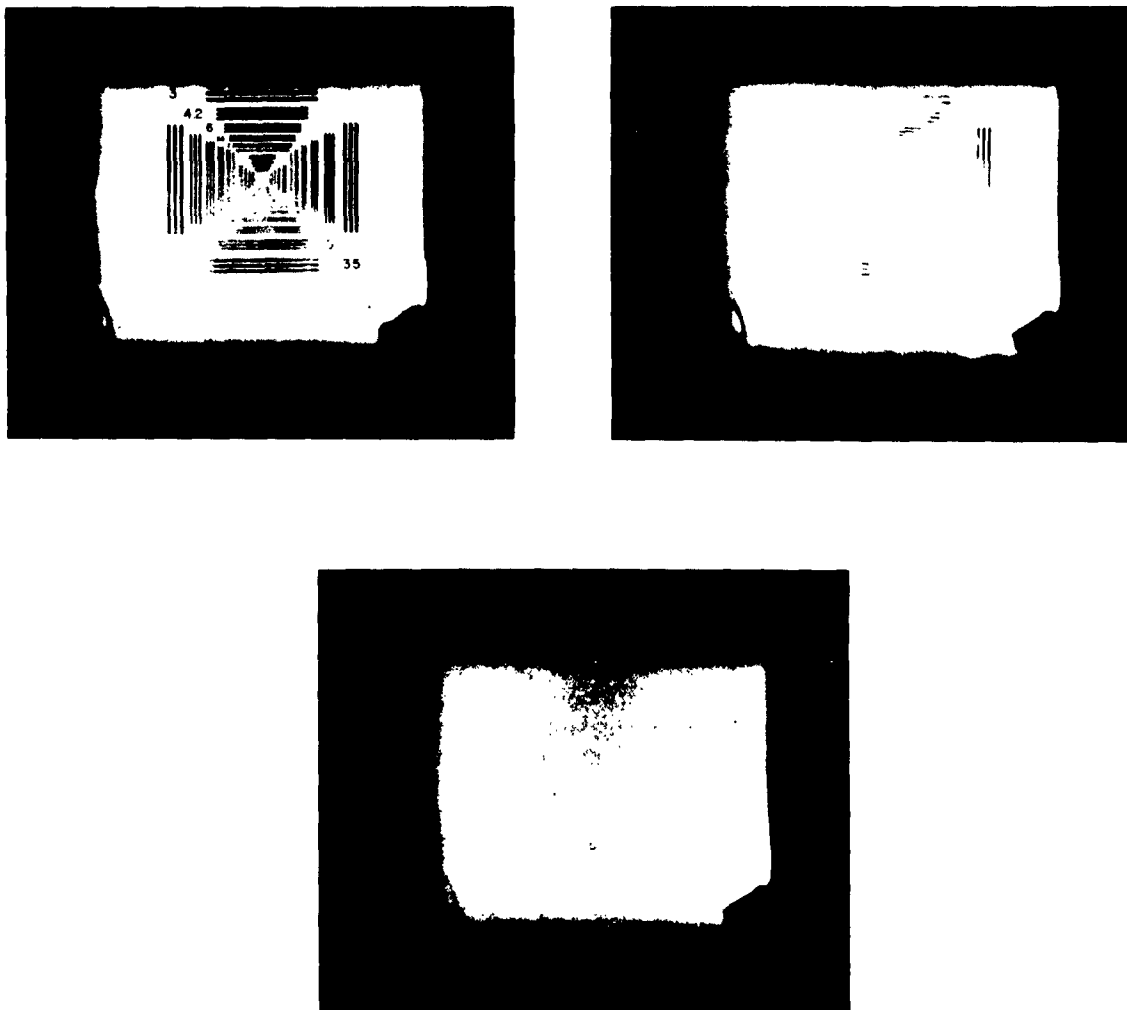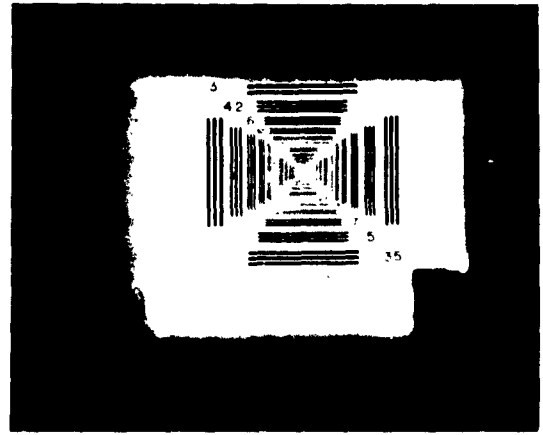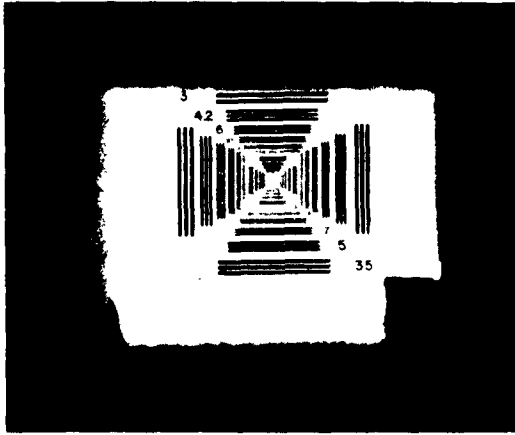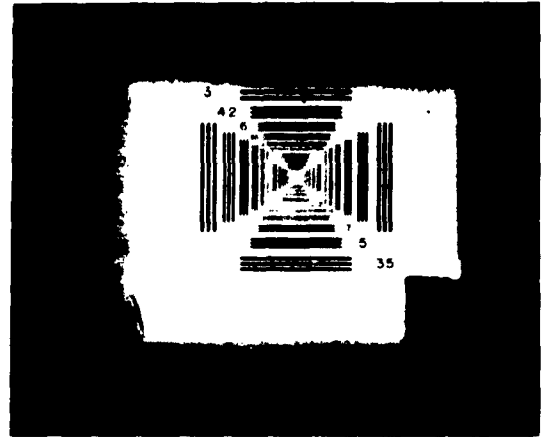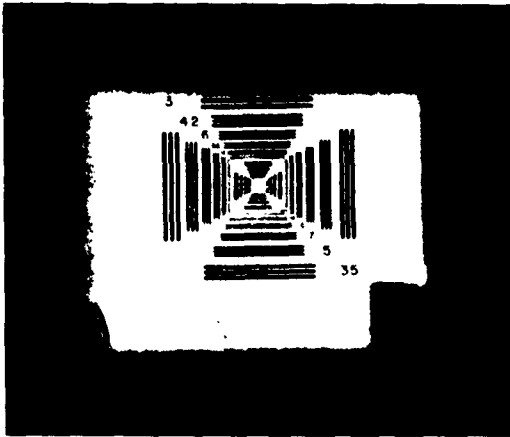Resolution Patterns of Acrylic Windows
Treated with PVA-Urea Formaldehyde

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Initial Exposure to High Humidity

Reexposure to High Humidity

Figure 15
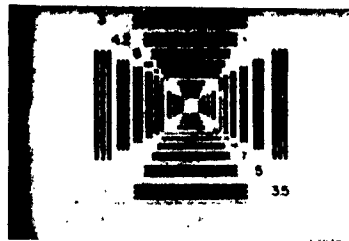Resolution Patterns of Acrylic Windows Treated with PVA-Formaldehyde

Another attempt to obtain PVA with partially blocked hydroxyl groups was made by alcoholysis of polyvinyl acetate (PVAc). This reaction was performed at 60°C in a 10% solution of PVAc (Gelva C-3, V-20) in methanol. Sodium hydroxide was added into the system from a methanol solution containing 0.015 g of sodium hydroxide per milliliter of methanol, until the total amounted to 10 meq of sodium hydroxide per gram of PVAc. After coagulation, the formed gel was broken into additional methanol and the mixture was neutralized with acetic acid. The precipitate, PVA, was washed, dried, dissolved in water and deionized in ion-exchange column containing Nalcite HCR and SB resin (Nalco Chemical Company) in a 1:2 ratio. Acrylic windows were treated by dip-coating with this PVA.

These treated windows showed slight surface imperfections which could be distinguished as tiny hills and valleys when viewed at oblique angles. The fog resistance of these samples was relatively poor, and visibility decreased appreciably during the first exposure to high humidity. Infrared measurements of the relative absorbencies for carbonyl and hydroxyl groups, obtained on mercury-cast films, indicated 95% hydrolysis of the alcoholized PVAc. Samples of PVA obtained by incomplete hydrolysis to PVAc and samples of formalized PVA showed 83 to 87% hydrolysis. These compounds, particularly those with a lower hydroxyl content, provided surface coatings with good optical properties even after exposure to 3 to 4 wetting-drying cycles.

On the other hand, coatings made from slightly hydrolyzed PVAc (12% hydrolysis) did not impart fog resistance to the substrate. This result was expected in view of the low concentration of hydrophilic sites on the deposited film. However, the same effect was observed on highly hydrolyzed PVAc and was substantiated in fogging tests performed on 98% hydrolyzed PVAc (Elvanol 72-51, E. I. du Pont de Nemours and Company). These results could be explained only by attributing the loss in hydrophilicity to pronounced hydrogen bonding of highly hydroxylated PVA.

Thus these observations demonstrated that the antifogging effectiveness of PVA films depends in great measure on the relative concentration of hydrophilic and hydrophobic surface groups.

The effect of temperature on the fog resistance of acrylic windows treated with partly formalized PVA was determined. Parallel experiments were carried out in which a treated window was conditioned for 15 hr at 65°C in an air-circulating oven and a similar specimen was maintained at 25°C. The results, shown in Fig. 16 and Fig. 17, suggest a slight improvement in the fog-resistance of the thermally treated sample. Both specimens exhibited incipient fogging in the third wetting-drying cycle. However, the sample subjected to heat cleared soon on continued exposure to condensing water vapor, while the room-conditioned sample retained a cloudy appearance. Hirabayashi (ref. 16) reported little change in optical properties of PVA on heating slightly above 100°C. At this temperature the optical degradation of the acrylic substrate would be pronounced.

First Exposure
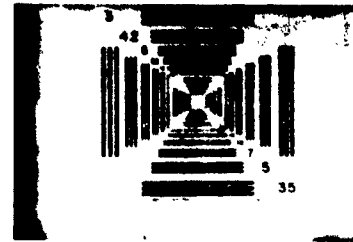
Second Exposure

Third Exposure

Third Exposure
15 Min Later

Figure 16
Resolution Patterns of Heated Acrylic Windows
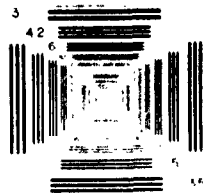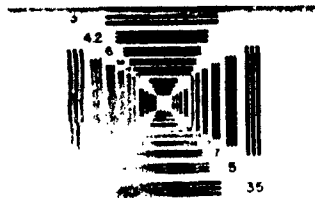Treated with PVA

First Exposure

Second Exposure

Third Exposure

Third Exposure
15 Min Later

Figure 17
Resolution Patterns of Room-Conditioned Acrylic Windows
Treated with PVA

F. Microscope Studies of the Condensation of Water Vapor on Treated Substrates

As a corollary to the optical investigations of the fog resistance of treated acrylic windows, a microscope study was conducted to obtain information on the location and activity of condensation sites on treated and untreated substrates. Measurements were made on the distribution, size, and separation of water droplets deposited on modified substrates at different temperature and humidity conditions. The Thomas-McCrone cold stage apparatus was used.

Unless the acrylic windows were scrupulously cleaned with detergent and subsequently with alcohol and distilled water, they exhibited a specific pattern of droplet formation which persisted in repeated exposures to high humidity. This pattern, compared with the random distribution of droplets on well-cleaned substrates, suggested that a residual compound was adsorbed on the surface of the acrylic. The residual compound presumably originated from the adhesive backing of the surface-protecting cover sheet.

On cleaned substrates the initial size of visible droplets was of the order of 5 μ in diameter. These droplets grew to approximately 12 μ before additional sites were activated, as evidenced by the formation of new, 5-μ droplets while the larger ones were still growing. Passage of additional moisture-saturated air resulted in coalescence of droplets. The minimum observable distance between droplets prior to coalescence was 6.5 μ.

A comparison of the condensation behavior of untreated and neutron-irradiated (2.2×10^4 n cm^{-2}) acrylic surfaces revealed slight differences in the initial diameter and droplet density of the condensate (Table 2). While droplets on the control slide formed in striations or at random, the irradiated sample exhibited aggregation of condensation droplets in clusters of two and three. However, the overall affinity of the irradiated material toward water vapor was much too small to promote adequate wetting of the substrate by the condensate.

Data on the condensation of water on other modified acrylic specimens are summarized in Table 2. Gelatin-coated slides adsorbed a continuous film of water on exposure to high humidity. The film structure was irregular, however, presumably as a result of the presence of discrete gel particles. The effectiveness of the Carboset 511-Nonic 218 system in providing a film with good optical properties on exposure to moisture was attributed to the activity of the surfactant (Nonic 218), since fogging tests performed with the water-soluble acrylic compound alone indicated its inadequacy in preserving good visibility. Surfactant-treated acrylic windows effected condensation of water over the entire surface of the specimen at high as well as low humidities. Similar results were obtained with 83 to 87% hydrolyzed PVAc coatings. The performance of surface-active agents stabilized by inclusion in gel-forming compounds, however, was less effective, as indicated by the drop-growth sequence on selected coating systems. It should be noted that temperature measurements made at the surface of samples were subject to error as a result of heat conduction along the thermocouple leads to the bead. Consequently, the microscopic observations of water condensation should not be

Table 2

DROPLET FORMATION ON TREATED ACRYLIC SUBSTRATES

Coating	Conditions at Top of Sample Temp., °F	R.h., %	Drop Size, 10^{-4} cm	Drop Spacing, 10^{-4} cm	Appearance
None (control slide)	58.5	55.8	10	10-20	
	58.5	58.0	20	10-20	
	58.5	63.5			Coalescence.
	58.5	71.0	60		
Gelatin	58.0	56.5		Irregular	Rapid growth to 40 μ.
	58.0	64.0			Condensation in clear areas.
	58.0	74.0			Coalescence and film formation.
Gelatin plus Polytergent B-350	58.0	37.6			Surface covered with striations.
	60.0	63.5			Film of water forming; striations fading.
	60.0	66.5			Complete film of water.
	51.0	34.0			Some condensation; discontinuities in coating.
	51.0	50.5			Water film forming; surface hazy.
	51.0	61.0			Brightness of microscope light diminished.
Carboset plus Nonic 218, 1:1 ratio	59.0	60.0			Film formation.
	59.0	68.0			Water film; continuous where coating uniform; coating dried poorly; surface patchy.
	49.0	96.0			Film formation; particles floating.
Titanium dioxide	56.0	53.5	1-10	10	
	56.0	59.5			Coalescence.
	56.0	70.0			80% of drops 80 μ or more.
	48.0	41.0	10	50	
	48.0	92.5			80-100% coalescence.
Irradiated sample	57.0	54.0	1	Clusters of droplets.	
	57.0	58.0	5-10	Coalescence of clusters.	
	57.0	67.5	80	10-20	
	48.0	44.5	10	Clusters of 2 and 3 droplets.	
	48.0	94.5	150	30-40	
Polyvox WSR-301 (Union Carbide Corp.)	58.0	47.0	1-5	10	
	58.0	53.5	10-20		
	58.0	70.0			Film formation; film distorts light.
	49.0	36.8			Some condensation.
	49.0	43.5			Film formation; poor visibility.
Gelatin plus Polyvox	60.0	53.0			Possible formation of film.
	60.0	54.0			Visibility of gelatin particles disappearing.
	60.0	63.0			Film irregular, causing poor visibility.
	49.0	52.5			Film appears to be composed of approximately 500-μ droplets.
Ethomeen-C/12, wiped, 1% solution Kelco Gel LV	50.0	29.0	6.5	6.5	
	50.0	100.0			Coalescence.
	57.0	32.0	6.5	6.5	
	57.0	36.5	13	6.5	
	57.0	100.0			Coalescence.
	59.0	48.0	13	6.5	
	59.0	53.5	13	6.5	
	59.0	56.5	20	6.5	
	59.0	63.0			Coalescence begins.
	59.0	70.5			75% of drops coalesced.
	59.0	87.0			Coalescence.
Sprayed 1% solution Gel LV	57.0	20.0	6.5	Along deposit border.	
	57.0	22.0	30	Along deposit border.	
	57.0	45.0	65	Along deposit border.	
	57.0	56.0			Coalescence begins; surface dried and temperature increased; circular gel deposits irregular.
	59.0	30.0			Film now on gel spots.
	59.0	51.0	6.5		Between gel spots.
	59.0	70.0			Coalescence begins.
Gel Lv, wiped, 1% solution Gel LV	38.0	--			Film froze and cracked.
1% solution Gel LV	62.0	10.0			Film streaked; no drops.
0.1 cc, Nonic 300	56.0	32.0			Film hazy; no drops.
10 cc Water	46.0	41.0			Crystals formed.
30% Cyanogum solution, 0.6 g Nonic 300	55.0	51.5			Film dissolved in water.

directly correlated with the juxtaposed calculated degree of water-vapor saturation.

G. Nucleation of Gas Phase to Induce Condensation

A brief feasibility study was conducted to determine the possibility of inhibiting fogging of helmet visors by preferential condensation of moisture inside the helmet enclosure. Data for a typical experiment are presented in Table 3. The increase in relative humidity after nucleation is due to reevaporation of the water from the sodium chloride nuclei into the main gas stream. The difference in the amount of water before and after nucleation compared with the quantity of water entering the visor determines the effectiveness of sodium chloride in promoting water-vapor condensation in the gas phase. The results presented in Table 3 indicate the possibility of removing water vapor from a gas phase by the nucleation method. Admittedly, the removal of moisture amounts to only a few percent. However, other sources of inorganic and organic materials could be found with a considerably greater nucleating ability than sodium chloride.

Table 3

RESULTS OF NUCLEATION OF GAS PHASE WITH SODIUM CHLORIDE

R. h. of airstream at 68°F: 72. 5% entering visor
42. 5% before nucleation
44. 0% after nucleation

Flow of water: 172×10^{-6} g/min entering visor
8.85×10^{-6} g/min removed from visor

Water removed: 5. 1%

Nuclei concentration: 3, 000, 000 parts/cc

Salt concentration in gas phase: 0. 42 g per gram of water

H. Determination of Optical Properties of Acrylic Visors

1. Luminous Transmittance

Luminous transmittance was calculated by integrating the product of spectral energy distribution of a source, the visual response of the C. I. E. standard observer, and the spectral transmittance of the test panel over the wavelength range of visible flux, as indicated by the following expression:

$$\text{Luminous Transmittance} = \frac{\int E_\lambda \, \bar{y}_\lambda \, T_\lambda \, d\lambda}{\int E_\lambda \, \bar{y}_\lambda \, d\lambda} \tag{6}$$

where

E_λ is the spectral energy distribution of the source, (C. I. E. Illuminant C Specified)

$\overline{y}_\lambda$ is the spectral sensitivity of the C. I. E. standard observer

T_λ is the spectral transmittance of the test panel.

The integrations were carried out by numerical methods because none of the functions are expressible in simple analytical form.

Since the sample compartment of the GE recording spectrophotometer which was used in these measurements was not large enough to accommodate finished visors, their transmittance properties were inferred from those of flat specimens. The results for different test panels are summarized in Table 4. The slight decrease in transmittance exhibited by a sample coated with partly formalized PVA in comparison with an untreated specimen is shown in Fig. 18.

Table 4

LUMINOUS TRANSMITTANCE OF ACRYLIC TEST SAMPLES

Sample	Luminous Transmittance
Untreated acrylic	0.918
Acrylic coated with Methocel 65 HG	0.923
Acrylic coated with 20% Gental	0.920
Acrylic coated with PVA	0.923

2. Haze

A hazemeter was assembled according to specifications of Method 3021, Fed. Spec. LP-406. Two transmission readings were taken: (1) total transmission with the test specimen close to the detector and (2) parallel transmission with the specimen 18 in. back from detector. Percent haze is defined as the difference of the two readings divided by total transmission and multiplied by 100. This difference represents the light flux which is scattered from the original beam. The precision of the measurement depends on the magnitude of the difference compared with that of the individual transmission values.

For highly transparent materials an upper limit of 3% haze is specified. Thus the instrument is required to measure two quantities of the order of 100 and 97, so that

$$\% \text{ Haze} = \frac{100-97}{100} \times 100 = 3. \tag{7}$$
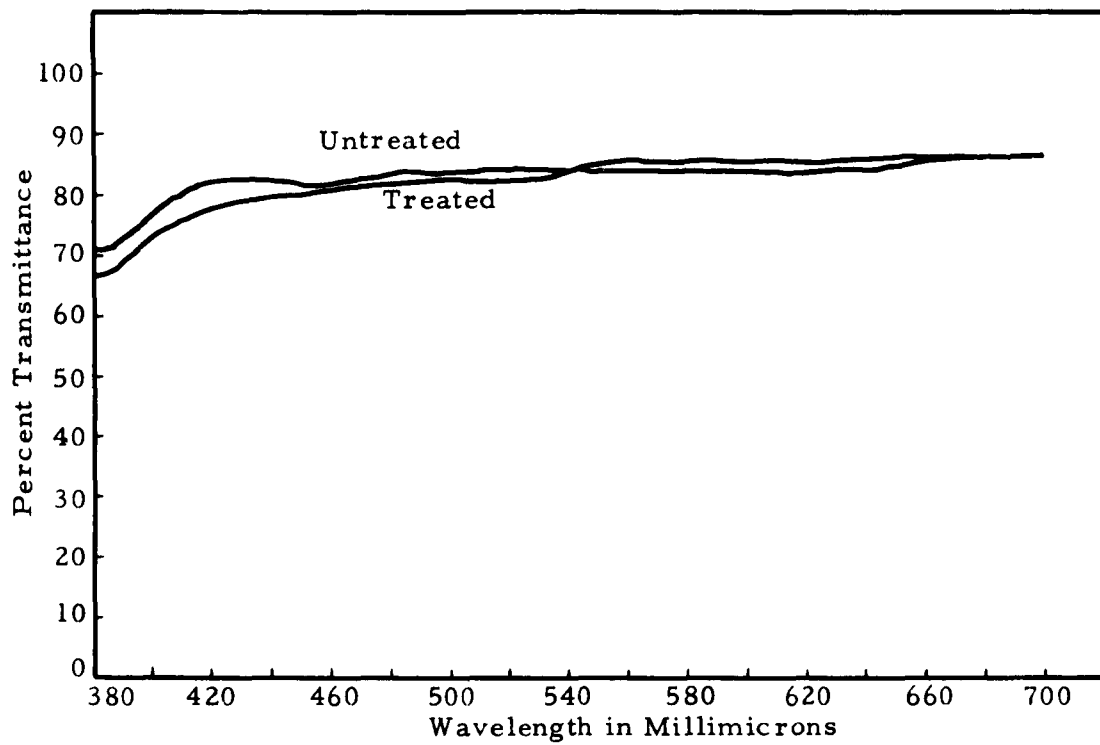
Figure 18
Luminous Transmittance
of PVA-Treated and Untreated Acrylic

Obviously, a small relative error in the transmission readings would result in a large relative error in the haze value. The reliability increases as the difference between transmission values increases.

Two alternative methods are inherently more precise and reliable for measuring low haze. They employ an integrating sphere for collecting and directly measuring the scattered flux. Two standard methods come under this classification:

(a) Method 3022, Federal Specification LP-406
(b) ASTM-D1003 49T.

The former uses a spectrally continuous source and the latter a GE recording spectrophotometer. Two quantities are measured in both cases: (1) total transmission and (2) scattered transmission. Percent haze is the second divided by the first. In order to measure the scattered flux, the straight-through light is trapped by a black cavity so that only the scattered component falls on the walls of the integrating sphere and is measured.

Data obtained on specimens evaluated by two methods are presented in Table 5. The reduced haze values obtained for some coated windows in comparison with the reference sample suggest a smoothing effect of the coating on the surface of the parent material.

Table 5

EVALUATION OF HAZE ON TREATED ACRYLIC WINDOWS

Specimen	Method 3021 Fed. Spec. LP-406			ASTM D1003 49T		
	% Total Transmission	% Parallel Transmission	% Haze	% Total Transmission	% Scattered Transmission	% Haze
Untreated acrylic	94.0	93.0	1.1	92.3	0.6	0.6
Acrylic coated with Methocel 65 HG	94.0	93.0	1.1	92.3	0.8	0.9
	93.5	93.0	0.5			
	94.0	93.0	1.1			
Acrylic coated with 20% Gental	95.0	93.5	1.6	92.0	1.3	1.4
	95.0	94.0	1.1			
	93.0	92.0	1.1			
Acrylic coated with PVA	--	--	0.4			

3. Optical Distortion

Measurements of optical distortion were performed according to Method 3041.1, Federal Specification LP-406. A projection lantern is focused on a white screen 25 ft away from the light source. When a test panel is held near and parallel to it, a shadow is cast on the screen. When the specimen is moved away from it in small steps, variations in the shadow are observed. If the panel is optically perfect, the shadow remains uniformly illuminated. If the panel contains imperfections, these show as dark and light patches as the specimen is moved away. The distance from the screen at which this occurs is a measure of distortion. Results obtained on treated acrylic windows are shown in Table 6.

Table 6

OPTICAL DISTORTION OF TREATED ACRYLIC WINDOWS

Specimen	Distance from Screen at which Patches Appear, in.			
	At Edges	At Isolated Central Areas	Over Entire Area	Visual Appraisal
Untreated acrylic	-	80	-	Good
Acrylic coated with Methocel 65 HG	2	7	20	Fair except for small checks.
Acrylic coated with Gental	-	-	1	Poor
Acrylic coated with PVA	-	70	-	Good

4. Prismatic Power

The unit of prismatic power is a prism diopter, defined as the power of a wedge or prism which produces 1 cm of linear deviation at a distance of 1 meter when the prism is operated at minimum deviation. This corresponds to an angular deviation of 0.01 radian, or 0.573 degrees, or 34.4 min. The test for prismatic power described in NBS Bulletin No. 533 consists of mounting a telescope 35 ft from a test chart on which are drawn concentric circles whose radii subtend known angles at the telescope. The resolution chart furnished with NBS Bulletin No. 533 contains two such circles whose radii subtend 1 and 2 min of arc, correspond to 1/32 and 1/16 prism diopters, respectively.

A chart was prepared with larger circles to correspond to 1/8, 1/4, and 3/8 prism diopters, since prismatic powers up to 0.25 were acceptable

for coated visors. The measuring procedure involved focusing the telescope on the concentric circles and adjusting the alignment until the center of these circles fell on the cross hairs of the eyepiece. The test panel was placed in front of the telescope, and the resulting displacement of circles was noted. The results are shown in Table 7.

Table 7

PRISMATIC POWER OF TREATED ACRYLIC WINDOWS

Specimen	Test Direction	Prismatic Power, diopters
Untreated acrylic	Diagonal	1/16
Acrylic coated with PVA	Diagonal	1/16
Acrylic coated with Methocel 65 HG	Diagonal	1/8
Untreated visor	Perpendicular to cylindrical axis	Negligible
PVA-treated visor	Both meridians	Negligible

5. Spherical Power

The unit of spherical or refractive power is a spherical diopter, defined as the reciprocal of focal length measured in meters. The test is described in NBS Bulletin No. 533. It makes use of the same telescope used for prismatic power with a resolution chart mounted at 35 ft. The telescope is first focused sharply on the resolution chart, and an index line is scratched on the draw tube to show the adjustment of zero power. Next a low-power lens of known power is mounted in front of the objective of the telescope and the telescope refocused. Another index line is scratched on the draw tube to correspond to the power of the lens used. In our case a 1/8 diopter lens was used, and the distance between scratch lines was accurately halved to represent 1/16 diopter.

The spherical power thus determined for untreated and PVA-coated MA-3 helmet visors, tested in a plane perpendicular to the cylindrical axis, was 0.12 diopters. This result agrees fairly well with the value obtained from calculations based on the data presented in Table 8.

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Table 8

DATA USED TO CALCULATE SPHERICAL POWER OF VISORS

Property	Value
Radius of front surface	4-7/8 in.
Radius of back surface	4-11/16 in.
Thickness	3/16 in.
Index of refraction	1.5
Calculated focal length	-8.5 meters
Calculated power	-0.118 diopters

I. Fog Tests in an Altitude-Simulating Chamber

To determine the antifogging effectiveness of partly formalized PVA coatings, tests were performed on MA-3 and HGU-8/P treated visors in a high-altitude facility at Wright-Patterson Air Force Base, under the supervision of Mr. Jerry Goodman of ASD.

In preliminary tests treated acrylic windows were inserted into a special mounting on an untreated MA-3 visor in such a way as to block a previously cut 3 x 4-in. opening and to provide pressure tightness in the helmet by the use of rubber gaskets around the circumference of the window. Thus only a small section of the composite visor was protected against fogging, and a convenient visual reference was provided for determining the effectiveness of the coating. Air Force personnel in a CSU-4P pressure suit and helmet tested the optical performance of the window in the space chamber, maintained at approximately -20°F. Although the untreated part of the compound visor fogged rapidly, the window section showed no adverse optical effects after 20-min exposure. On repeating this experiment with the same window, after equilibrating the visor at room temperature, the window again showed little change in optical properties, while the surrounding acrylic lens exhibited severe effects of fogging and distortion. Fogging and distortion also occurred in tests performed on treated MA-3 visors after two test cycles.

The optical performance of treated and untreated visors was evaluated under simulated use conditions. The temperature in the test chamber was gradually lowered, and observations of the visual clarity of the acrylic lens were made while the suit was pressurized to 6 mm Hg above ambient conditions. Results obtained in the first run at a chamber temperature of 106 to 27°F are summarized in Table 9. Visibility through a visor treated with partly esterified PVA remained relatively good in spite of continuous water-vapor condensation on its surface. A visor treated with a commercial antifogging solution fogged after prolonged exposure. This could be partly attributed to a malfunction of the exhalation valve, which increased the helmet pressure to 12 mm Hg and affected the breathing rate of the helmet wearer during the test. The reference helmet visor fogged severely, and condensation of discrete water droplets caused appreciable distortion.

Table 9

VISUAL OBSERVATION OF OPTICAL CHANGES IN TREATED AND UNTREATED HELMET VISORS

Exposure, min	Avg. Temp. in Chamber, °F	Untreated Visor Surface Temp., °F		Visual Effects	Visor Treated with Coml. Cpd. Surface Temp., °F		Visual Effects	Visor Treated with Modified PVA Surface Temp., °F		Visual Effects
		Outside	Inside		Outside	Inside		Outside	Inside	
0	106	104	102	-	105	103	-	106	104.5	-
20	106	-	-	-	103	102	-	104	102.5	-
63	63	76	88.5	Light condensation of water vapor.	83	91	Thin water film forms in center of visor.	78	87	No change.
69	61	70	83.5	Medium-heavy film of water.	80	88	Water droplets and light film of water.	74.5	83.5	Small droplets in center area of visor.
87	45	56	74	Light fog, water droplets.	70	84	Light fog in center, heavy fog at circumference.	64.5	77	Light film of condensed water.
103	43	46	69	Medium-heavy fog, water droplets.	66	74	Medium-heavy fog.	53	67	Light film of condensed water.
113	40	47	68	Severe fog, water droplets.	60	74	Severe fog.	53	64	Medium-heavy film of condensed water.
127	27	45	65	Distorted vision.	64	69	Almost no vision.	52	60.5	Medium-heavy film of uniformly condensed water.

In subsequent tests performed with the same visors the temperature of the chamber was lowered to -50°F. The acrylic lens coated with modified PVA maintained relatively good visibility until the inner surface of the visor reached a temperature below the freezing point of water. At this point the uniformly condensing film of moisture solidified, assuming the appearance of frost. This occurred after 30 min of rapid cooling, during which the temperature of the test facility dropped from 88 to -25°F. It was observed that forced breathing against the visor helped the wearer to melt the frost and partly restore vision. When the temperature of the chamber was raised from below 0 to 50°F, the visor recovered its optical clarity and maintained it as the outside temperature decreased to -30°F. Under equivalent conditions the untreated visor showed effects of intermittent fogging and frosting. Under all the test conditions visibility through the untreated visor was drastically reduced.

V. SUMMARY AND CONCLUSIONS

This investigation was concerned with the development of methods for preventing visibility losses due to fogging of high-altitude helmet visors. Attention was directed to the modification of surface properties of plastic visors and to the inhibition of fogging by preferential condensation of moisture inside the helmet enclosure by gas-phase nucleation. The second approach, in which vaporized sodium chloride condensation nuclei were utilized, was not effective; only 5% moisture was removed from the helmet enclosure.

To evaluate various treatments for modifying the surface of visors, a test apparatus capable of maintaining differential temperature and humidity conditions within +95 to -50°F and 20 to 95% r. h. was developed. The optical quality of treated acrylic windows exposed to fog-promoting conditions was measured by the optical resolution of a line pattern photographed through the window. Microscope studies of the distribution and activity of condensation sites on treated and untreated acrylic surfaces indicated preferential condensation of water vapor on active centers of the substrate. These sites were widely scattered and randomly distributed on well-cleaned untreated windows. The size and number of droplets formed on treated acrylic windows varied inversely with the effectiveness of the treatment.

Physical methods of enhancing the wettability of acrylic surfaces by ultraviolet irradiation and exposure in a thermal column of a nuclear reactor were ineffective. Samples exposed in the reactor exhibited a pronounced yellow discoloration, which markedly reduced the luminous transmittance of the plastic.

Cationic and nonionic surfactants reduced the tendency to fogging of treated visors. However, the effectiveness of these compounds diminished greatly on prolonged and intermittent exposure to high humidity.

Hygrophilic film-forming polymers, particularly those with polyhydroxyl groups, appeared promising as fog-resistant coatings because of their relatively good optical quality and antifogging activity. Efforts were

made to increase the durability of modified polyvinyl alcohol coatings by converting the PVA solution into a thermally reversible gel and by balancing the acyl/hydroxyl ratio through controlled formalization of PVA or hydrolysis of polyvinyl acetate. Infrared spectrophotometric measurements indicated that partly esterified (83 to 87% hydrolyzed) PVA films kept the acrylic windows fog-free when subjected to repeated wetting-drying cycles. Tests conducted at Wright-Patterson Air Force Base in a chamber simulating high altitude indicated relatively good optical performance of treated MA-3 and HGU-8/P helmet visors on intermittent exposure to differential temperature and humidity conditions. However, the exhalation vapors, which originally did not interfere with vision, solidified when the external temperature dropped to -30°F. The frost which formed at the inner surface of the visor reduced visibility. When the frost was dissipated at elevated temperatures, the treated surface recovered its antifogging activity.

Lack of appropriate care in handling the treated visor during moisture condensation under conditions of use, such as accidental rubbing of the wet surface, could result in deterioration of optical properties of the visor.

Although the polymeric treatment developed for acrylic vision devices proved relatively satisfactory in laboratory tests, its ultimate capability cannot be fully realized without additional, precise data on the relationship between (1) effectiveness and durability of the treatment and (2) composition and structure of the treating agent. Such information would further the development of an antifogging compound with optimum surface reactivity toward water vapor and concomitant resistance to solvation by the condensate.

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